

Deciphering Ni sequestration in soil ferromanganese nodules by combining X-ray fluorescence, absorption and diffraction at micrometer scales of resolution

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Soils are a major sink for anthropogenic Ni, and its migration to living organisms is an environmental concern because of its suspected carcinogenicity when it is speciated as nickel sulfate or combinations of nickel sulfides and oxides, provoking lung and nasal cancers. The anthropogenic nickel sources are the metal processing operations, the combustion of coal and oil, and amendments by sewage sludge. The crystal chemistry of nickel in oxidized and silicated ores has been abundantly studied for economic reasons, and in these formations Ni is predominantly associated with phyllosilicates and the Fe oxyhydroxide, goethite (α -FeOOH). During its journey from the source to its resting place in soils, Ni can undergo many chemical transformations, and understanding how this element is naturally sequestered helps provide a solid scientific basis for maintaining soil quality and formulating educated strategies to remediate severely impacted areas. The most efficient and durable process responsible for trace metal sequestration in soils is the formation of ferromanganese micronodules, which often have been compared to the well-known oceanic Mn nodules. In this work, we have studied how nickel is sequestered in soil nodules from the Morvan region (France) by combining, for the first time, scanning X-ray microfluorescence (μ SXRF), microdiffraction (μ SXRD), and extended X-ray absorption fine structure (μ EXAFS) spectroscopy, all applied at the micrometer-scale of resolution. The two first techniques were used to identify the host solid phase by mapping the distributions of elements and solid species, respectively. μ EXAFS was then used to determine the mechanism of Ni binding by the host phase at the molecular scale. We showed that nickel substitutes for Mn^{3+} in the manganese layer of the MnO_2 - $\text{Al}(\text{OH})_3$ mixed-layer oxide lithiophorite. The affinity of Ni for this mineral was subsequently found to be characteristic of micronodules sampled from soils across the USA and Europe. Since many natural and synthetic materials are heterogeneous at nanometer to micrometer scales, the unprecedented synergistic use of μ SXRF, μ SXRD, and μ EXAFS is expected to have broad applications to earth and materials science.

RESULTS AND INTERPRETATION

With μ SXRF (three first maps) the distribution of Fe, Mn, and Ni were first determined, and it was found that Mn and Ni were systematically associated in the six different soil nodules examined in this study. Then, mineral abundance maps were produced by integrating at each point-of-analysis the diffracted intensities of the non-overlapping (020) and (200) reflections at ~ 4.45 Å and ~ 2.57 Å for phyllosilicate, the (101) and (301) reflections at 4.19 Å and 2.69 Å for goethite, the (001) reflection at 7.1-7.2 Å for birnessite, and the (001) and (002) reflections at 9.39 Å and 4.69 Å for lithiophorite. The reliability of this quantitative treatment was verified by comparing mineral maps calculated using independent (hkl) reflections of the same mineral species. The distribution of Fe-vernadite, a common soil mineral, was not mapped because it was systematically detected throughout the examined nodules without significant gradient of concentration. This Fe-Mn disordered phase (also termed Mn-feroxyhyte), that is dispersed throughout the nodule matrix filling pores and aggregating coarse grains, acts as a cementing agent for the nodules.

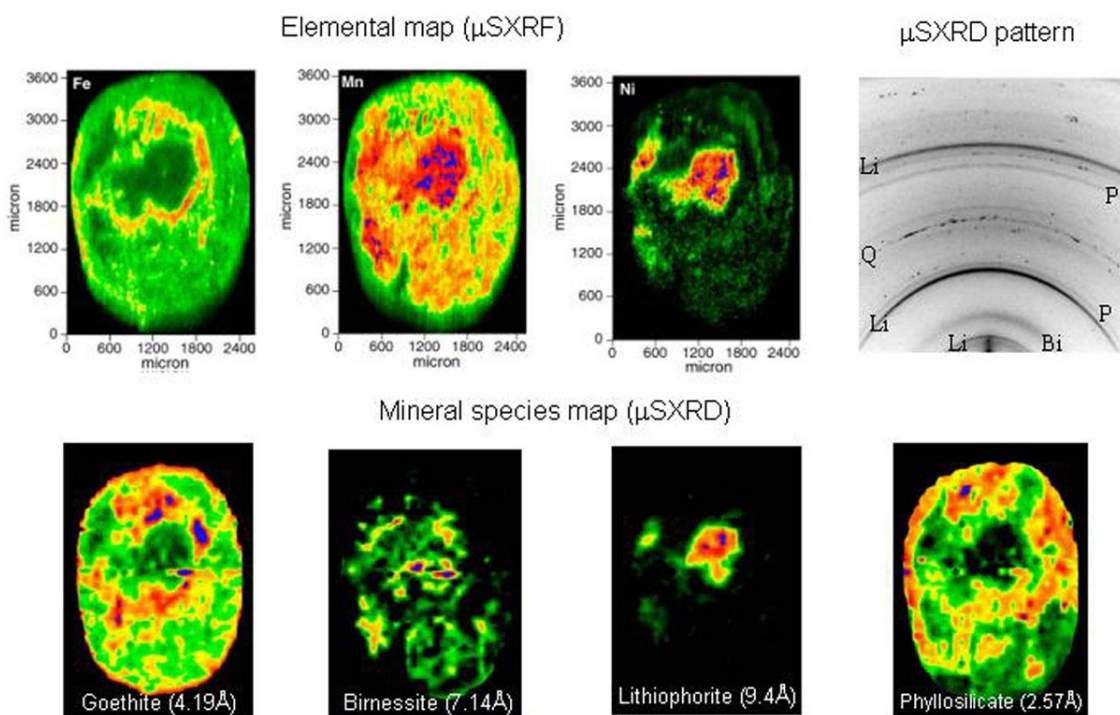


Figure 1. Combined fluorescence - diffraction measurements recorded at Beamline 7.3.3. on a ferromanganese soil nodule. The three images on the top are elemental maps obtained by μ SXRF, and the four images on the bottom are mineral species maps obtained by integrating at each point of analysis the intensities of the relevant (hkl) reflections along the Debye rings of the two-dimensional XRD patterns (d-spacings are indicated in parenthesis). One XRD pattern is presented to the top right. Li = lithiophorite, Bi = birnessite, P = phyllosilicate, Q = quartz.

The comparison of the μ SXRF and μ SXRD maps clearly shows that nickel and lithiophorite have the same contour maps, therefore suggesting that Ni is bound to this particular mineral phase. The systematic association of Ni-lithiophorite suggests that Ni should be located in a definite cation site of the manganese oxide crystal structure. To determine the Ni site, Ni K-edge μ EXAFS spectra were collected on Beamline 10.3.2. in Ni 'hot spots' from several nodules. All spectra were identical, indicating that the incorporation mechanism of nickel is unique, and is the key to understanding its sequestration in soils. Qualitative information about the local structure of Ni can be obtained by comparing the unknown μ EXAFS spectrum to reference EXAFS spectra from relevant model compounds. As expected from μ SXRF – μ SXRD experiments, the two reference spectra for Ni in goethite and phyllosilicate did not match the unknown spectrum, confirming that Ni is not sequestered in these forms (data not shown). Differences in frequency and shape of the EXAFS oscillations were also observed with birnessite, in which Ni is sorbed above vacant Mn sites, and with lithiophorite, in which Ni is located within the gibbsitic Al layer (Fig. 2a). The radial structure functions (RSFs) obtained by Fourier transforming EXAFS spectra for the reference and the soil lithiophorite both exhibit, after the first oxygen peak, a second peak at roughly $R + \Delta R = 2.6 \text{ \AA}$, that is at a distance characteristic of edge-sharing linkage between metal octahedra (Fig. 2b). This result alone suggests that Ni is located within one of the two octahedral layers of the lithiophorite structure. To solve this alternative, suffice it to examine the phase of the imaginary part of the Fourier transform, because waves backscattered by Al and Mn atoms are almost out-of-phase. Examination of Fig. 2c shows that the unknown and lithiophorite reference have their electronic waves shifted by $\sim \pi$ in the $2.2 - 3.1 \text{ \AA } R + \Delta R$ interval, thus indicating that Ni is substituted for Mn in the soil lithiophorite. In keeping with this conclusion, the two waves

are logically in phase in the 1.0 – 2.2 Å $R + \Delta R$ interval, since in both structures Ni is octahedrally coordinated to oxygen atoms.

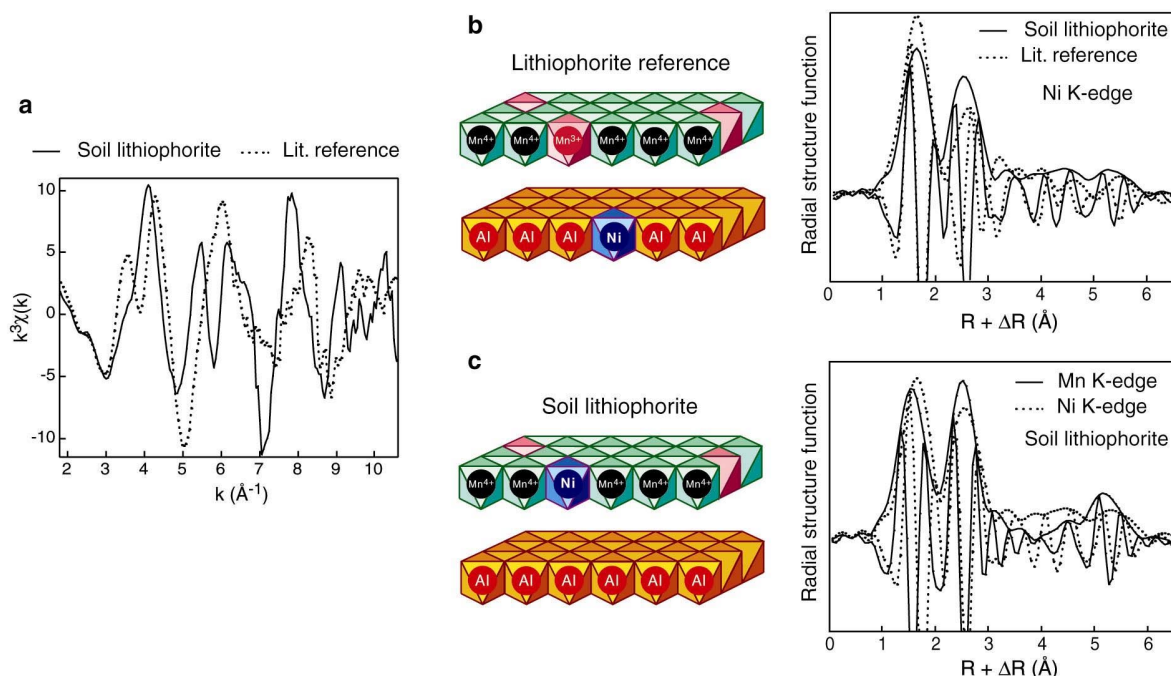


Figure 2. Ni K-edge μ EXAFS spectrum (a) and Fourier transform (modulus plus imaginary part) (b,c) from a ‘hot spot’ of the core of the nodule, compared to the Ni- and Mn-edge data from a Ni-containing lithiophorite reference, in which Ni substitutes for Li in the $\text{Al}(\text{OH})_3$ layer. Data were collected on Beamline 10.3.2.

Since Ni^{2+} has an effective radii 30% greater than Mn^{4+} , one may wonder how the Ni-Mn substitution is realized. To answer this question, Ni- and Mn-RSFs were plotted together (Figure 2b, bottom right), and the Ni- and Mn-EXAFS interatomic distances compared. A distinct feature in the Ni-RSF is the shift to higher $R + \Delta R$ values of the Ni-O peak, indicative of a relaxation of the Ni site owing to the larger ion size of the Ni^{2+} impurity ($r = 0.69$ Å) relative to Mn^{4+} ($r = 0.53$ Å) and Mn^{3+} ($r = 0.645$ Å). Since Ni^{2+} and Mn^{3+} have a size mismatch of only 7%, nickel likely substitutes on the trivalent manganese site. Likewise, the Al^{3+} site of the gibbsitic layer is clearly too small ($r = 0.535$ Å) to accommodate Ni^{2+} , and the larger Li^+ site ($r = 0.76$ Å) is probably energetically less favorable. This assumption is supported by recent atomistic calculations and EXAFS measurements on lanthanide-doped perovskite, which showed that the rare earth is energetically stabilized in smaller crystallographic sites. A best fit to our data was given by octahedral coordination of nickel with oxygen at 2.05 Å and six manganese at 2.91 Å, and average Mn-O and Mn-Mn distances of 1.92 Å and 2.92 Å, respectively. There was no indication of Ni-Ni pairs, for which Ni-Ni distances of 3.03 Å to 3.12 Å would be predicted. This result indicates that nickel did not precipitate as a hydroxide, hence confirming that the next-nearest coordination shell of Ni is made of Mn atoms. Similar results were obtained on nodules from flood plain soils in the USA, which suggests that the Ni species identified herein may correspond to a major sequestration form of Ni in Earth near-surface environments.

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